BACKGROUND INFORMATION

Introduction

The Department of Water Resources has participated in or sponsored investigations involving agricultural drainage water since early 1960. Selenium in agricultural drainage water became a concern in the 1980s with problems at Kesterson National Wildlife Refuge in Merced County. Birth deformities and deaths of aquatic birds at the refuge were attributed to the accumulation of selenium in the refuge's water and soils. The refuge was operated as a staged evaporation basin complex for drainage water while documentation was being prepared to complete the San Luis Drain. Discharge of drainage into the refuge terminated in 1985. The San Luis Drain was closed a year later.

The San Joaquin Valley Drainage Program was established in 1984 to address drainage and drainage-related problems and impacts of drainage activities on the environment. In 1990, the SJVDP, a joint federal and State effort, recommended further development of the "Binnie Process" to reduce or remove selenium from drainage water. This process employs an anaerobic treatment or a combination of anaerobic treatments in series followed by filtration. Development of this process led to the establishment of the Adams Avenue Agricultural Drainage Research Center near Tranquillity, California.

In September 1990, the Adams Avenue project commenced as a cooperative effort among DWR, United States Bureau of Reclamation, Westlands Water District, and the Engineering Research Institute at the California State University, Fresno to provide a facility to develop and field demonstrate processes to treat agricultural drainage water. Testing began in September 1992 and ended November 1995.

Processes and Treatment Trains Tested

At one time, seven processes were operated at the Adams facility. These processes included an upflow anaerobic sludge blanket reactor (UASBR), two fluidized bed reactors (FBR 1 and 2), two slow sand filters (SSF 1 and 2), a packed bed reactor (PBR), and a pilot upflow anaerobic sludge blanket reactor (UA2). The processes were arranged in two treatment trains consisting of an UASBR/FBR1/SSF1 (Train 1) and UASBR/SSF2 (Train 2). The FBR2, PBR, and UA2 processes were operated as stand-alone processes. A schematic of the process trains and processes tested at the Adams facility is shown in Figure 1. Also, laboratory-scale investigations were performed at the CSUF campus to develop start-up parameters when the infrastructure for the facility was being developed and constructed. These investigations tested a sequencing batch reactor, a UASBR, a packed bed reactor, and slow sand filtration processes.

Laboratory-scale investigations at the CSUF campus to develop start-up parameters commenced in August 1991 and were completed October 1992. UASBR began operating in September 1992 and continued until closure of the Adams facility in November 1995. Testing was interrupted for two periods, from April 1993 to July 1993 and from August 1993 to September 1993, for system modifications and repairs. The fluidized bed reactors were brought online in October 1993 and remained in operation until November 1995. The slow sand filters were operated from

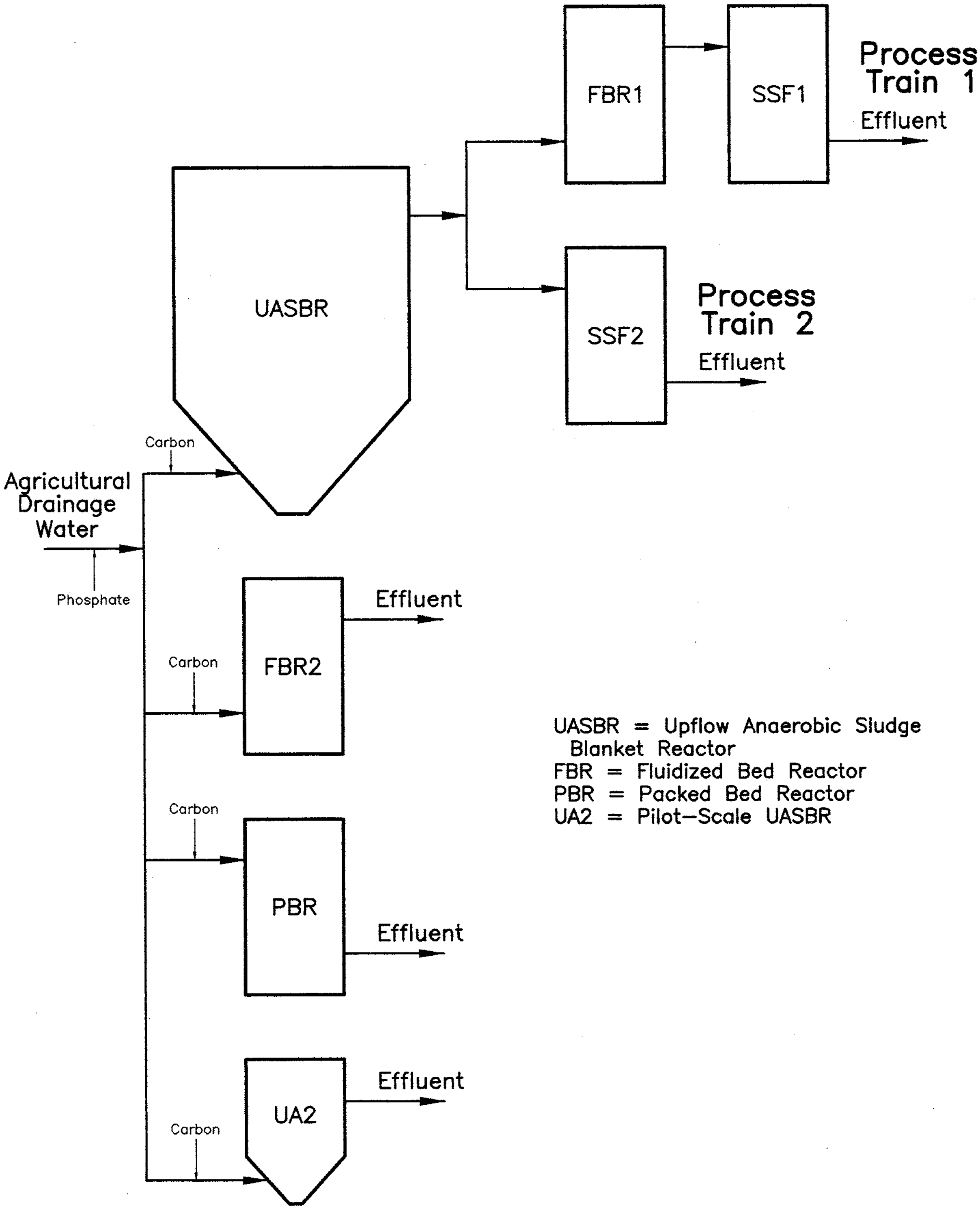

Figure 1. Process Trains and Process Tested at the Adams Avenue Facility

October 1993 to November 1994. Testing with the UA2, the pilot UASBR, began June in 1994 and ended in November 1995.

Anaerobic Treatment Processes

The sludge blanket reactor and fluidized bed reactor processes were the anaerobic processes tested by EPOC AG and Binnie California, Inc. at Murrieta Farms and by CSUF at the Adams facility. Anaerobic processes are used in a wide variety of applications. Anaerobic digestion is commonly used to stabilize municipal sewage sludge. Other applications include removal of organic constituents in high-strength industrial wastewaters in pulp and paper, food processing, and beverage industries. Use of these processes is also being developed to treat low-strength wastewaters. The work at Murrieta Farms and the Adams Avenue facility were initial developments of anaerobic processes to reduce and remove selenium from agricultural drainage water.

Anaerobic treatment involves decomposing organic and inorganic material in the absence of oxygen. In a closed system, anaerobic bacteria break down complex organic compounds into more basic ones. Advantages of anaerobic treatment processes include a low production of waste biological solids, low nutrient requirements, no energy requirements for aeration, high loading rates that can be applied under favorable conditions, and anaerobic sludge that can be stored unfed for many months. Disadvantages of the processes include long periods of time required for start-up, high-sensitivity to specific compounds, and little operating experience exists on the application of the process to the direct treatment of wastewater (Lettinga and others 1980).

Selenium: A Brief Description of the Element and Commercial Uses

Selenium is the thirty-fourth element in the Periodic Table of Elements. This nonmetallic element is in the sulfur family and resembles sulfur in its various forms and compounds. Elemental selenium is considered a trace element and is thought to be non-toxic. Other valence forms of selenium are selenate (+6), selenite (+4), and selenide (-2). Selenate is the most soluble form of selenium. Selenium in agricultural drainage water is 85 percent to 95 percent in the selenate form.

Selenium is an element required by humans and livestock in trace amounts to maintain a healthy diet. It is an essential antioxidant for humans. The soil of various areas on the east side of the San Joaquin Valley is selenium deficient and selenium must be added as a supplement to cattle feed to prevent white muscle disease. Excessive selenium in livestock can cause improper bone development, alkali disease, and cerebral disorders. The effects on wildlife of an excessive amount of selenium were demonstrated at Kesterson Wildlife Refuge as previously noted.

Commercially, selenium is widely used in the glass, photographic, reprographics, and electrical industries. It is used to decolorize glass and to make ruby-colored glasses and enamels in the glass industry; produce photocells, photograph exposure meters, and solar panels in the photographic industry; reproduce and copy documents, letters, and other materials in the reprographics industry; and used in the electrical industry in rectifiers and to convert alternating current electricity to direct current electricity.

Selenium Analyses

Selenium analyses for the Adams Project were performed according to Standard Methods procedure 3500-Se C, a continuous hydride generation/atomic absorption spectrometric method. The Hydride generation method involves the addition of a strong reducing agent (sodium borohydride) to the sample to generate a gaseous hydrogen selenide. The gas is swept into a heated quartz cell aligned in the optical path of an atomic absorption spectrophotometer equipped with a selenium lamp operating at 196 nm. The signal produced by the gaseous hydrogen selenide is proportional to the amount of selenite present in the sample. A Varian SpectraAA-10 flame absorption spectrophotometer equipped with a VGA-76 vapor generation assembly and a PCS-56 automatic sampler was used for the analyses. The detection limit for the apparatus is 1 ug/L.

Three analyses were performed on most of the samples. Total selenium was measured by first oxidizing all species to the selenate form (Se^{+6}) with potassium permanganate. The selenate was then reduced to selenite with hot hydrochloric acid. Soluble selenium was similarly treated to total selenium, except the sample was filtered through a 0.22 um nylon membrane filter to remove particulate selenium prior to the oxidation step. Selenite (Se^{+4}) was determined from the sample directly without digestion, since this is the valence state from which the selenium hydride is formed.

A duplicate sample, a spiked sample, and a spiked blank were analyzed with each type of selenium determination for each sample set. The control limits were +-15% RPD for duplicates and +-20% for recovery of the spiked samples. Sample sets which did not pass the QC limits were repeated until they passed, to a maximum of three times. After the third run, if the QC values were not satisfied, judgment on which was the best value based on the historical concentration of each form of selenium in each sample was used to select the best representative analysis set.

For the discussion of selenium results in this report, total selenium refers to the concentration of all selenium species in the sample before filtration, soluble selenium is a measure of total selenium after passing through a 0.22 um laboratory filter, selenite is the concentration of selenium in the +4 valence state without the sample pretreatment steps, and particulate selenium is the difference between the total and soluble values. The relationship between the measured selenium values and the possible selenium species that might be incorporated in that measured value is shown below in Table 1.

Table 1
Relationship of Measured Selenium Values to
Possible Selenium Species

Measured Selenium Value	Selenium species that may contribute to the measured value
Total Selenium (Total Se determined for an unfiltered sample)	**Particulate Species:** Elemental Se, Se incorporated into bacterial cells or other particulates **Soluble Species:** Selenate, selenite, dissolved organic selenium (such as selenoamino acids) Notes: 1. Represents all Se species present in the sample. 2. Total Se = Particulate + Soluble
Soluble Selenium (Total Se determined for a sample after passing through a 0.22 μm membrane filter)	Selenate, selenite, dissolved organic selenium, any particulate selenium capable of passing through a 0.22 μm filter
Selenite	Selenite only

Notes: Selenate selenium is in the +6 oxidation state and the oxyanion is SeO_4^{-2}. Selenite selenium is in the +4 oxidation state and the oxyanion is SeO_3^{-2}. Elemental selenium is in the 0 oxidation state. The table above was obtained from *AAADRC Operation Report* September 1992 - December 1994.

Nitrate Analyses

Throughout the entire testing period, field nitrate analyses were performed using a colormetric method from Hach Company. The field analyses compared well with weekly laboratory analyses initially performed by the nitrate electrode method - Standard Methods procedure 4500-NO3 C. Unfortunately, a bias was found in August 1995 when nitrate was determined by ion chromatography. The field analyses provided a low bias on the untreated water and a high bias on the treated water. The UASBR's influent and effluent averaged 65 and 2.1 mg/L as N, respectively, as determined by the laboratory ion chromatographic (IC) method, while field determinations averaged 35 mg/L as N and 6.0 mg/L as N for the same period from August 1, 1995 to November 21, 1995. Such bias was also shown by comparing FBR2's and the PBR's the average effluent nitrate analyses for the two methods. Even though this bias exists, field measurements are used for evaluation in the report.

Agricultural Drainage Water

The agricultural drainage water treated at the Adams facility was subsurface drainage obtained from Westlands Water District's collector drain 136.0. The drainage water was taken from a collector sump alongside Lincoln Avenue and pumped 6,200 feet through 6-inch, Class 125 PVC pipe into a 6,000-gallon storage tank at the Adams facility. Potassium phosphate was added to the drainage water to ensure a sufficient amount of nutrient for biological growth. The constituent concentration makeup of the Adams drainage water was similar to that of

San Luis Drain water. Table 2 compares constituent concentrations from a sampling station on the San Luis Drain to drainage water tested at the Adams facility.

Table 2
Agricultural Drainage Water Constituents

	San Luis Drain*	Adams**	
Nitrate	47	30	mg/L as N
Nitrite	0.04	na	mg/L as N
Alkalinity	191	191	mg/L as CaCO3
pH	8.2	7.5	
Selenium	261	520	ug/L
Total Suspended Solids	na	19	mg/L
Volatile Suspended Solids	na	10	mg/L
Total Dissolved Solid	9,471	8,311	mg/L
Total Organic Carbon	9.3	12.4	mg/l

*Average of Monthly Values of San Luis Drain at Bass Road from 3-82 to 12-85
**Adams Avenue Average Values
na - not available

Location, Site Development, and Infrastructure

The Adams facility was adjacent to the San Luis Drain at 29177 West Adams Avenue near Tranquillity, in western Fresno County, as shown in Figure 2. The property is in an area of shallow flooding and owned by Westlands Water District.

In 1988, WWD chose the Adams site for two of its projects (a deep well injection project and a 1-mgd prototype selenium removal plant) to resolve agricultural drainage problems. These projects were never fully developed due to results for the exploratory test well and lack of funding for the treatment plant.

The infrastructure of the Adams facility was developed in a coordinated effort by WWD, Engineering Research Institute, and DWR. Site development included construction of an elevated, engineered earth pad on which the facility was built; placement of a paved roadway; installation of electrical power and control panels, switchgear, and wiring; relocation of personnel trailers, workshop sheds, equipment, tanks, and other items and materials from DWR's Los Banos desalting facility; construction of the drainage water supply and effluent lines; installation of a service water system; and other work to make the facility functional. Completion of the drainage water supply line in June 1992 signified that the core of the infrastructure work was complete. The infrastructure layout for the Adams facility is shown in Figure 3.

Laboratory-Scale Investigations

When the infrastructure of the Adams facility was being developed and constructed, and the equipment was being installed, CSUF performed on-campus, laboratory-scale investigations to develop start-up operation parameters for the processes proposed for testing at the Adams

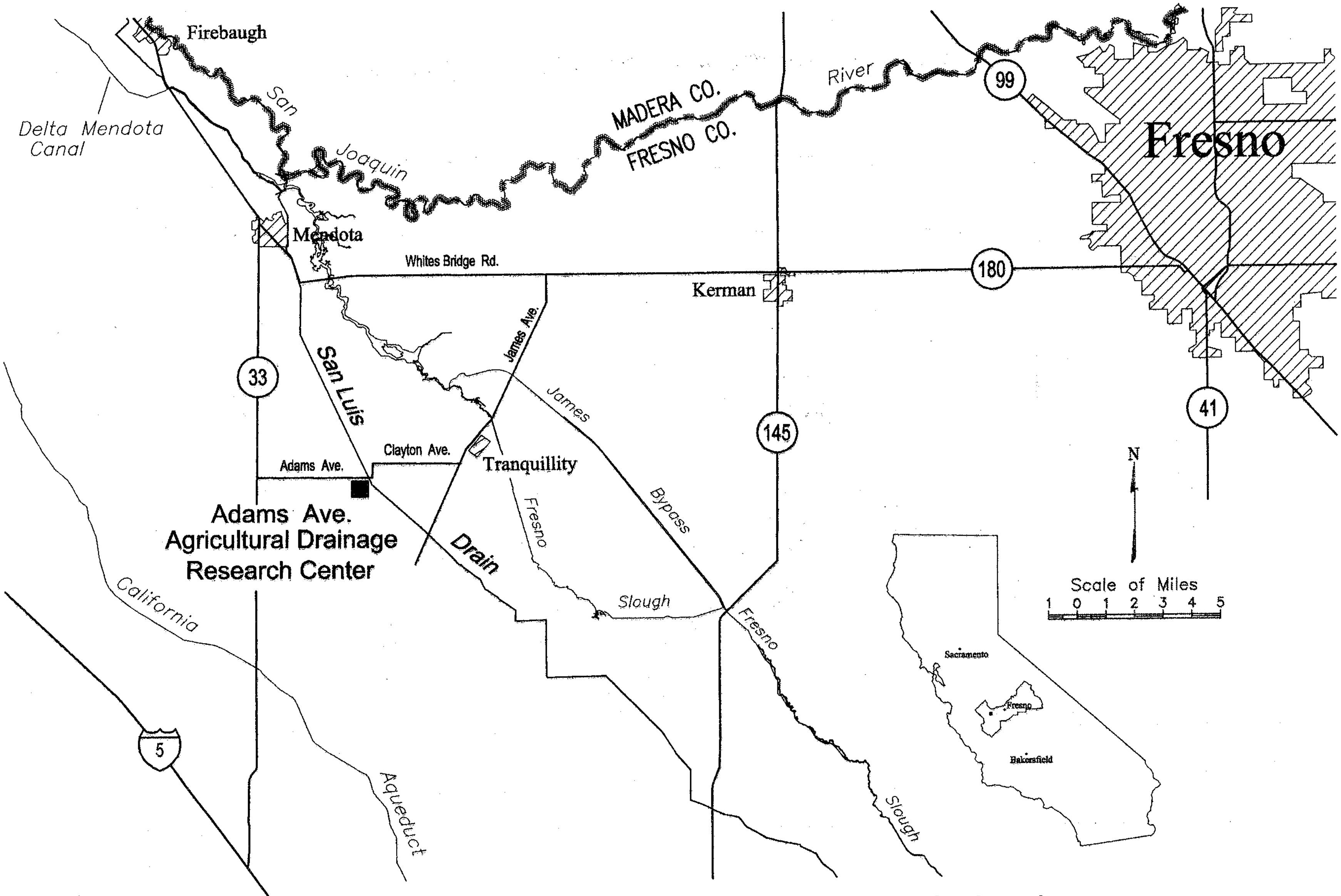

Figure 2. Location of the Adams Avenue Agricultural Drainage Research Center

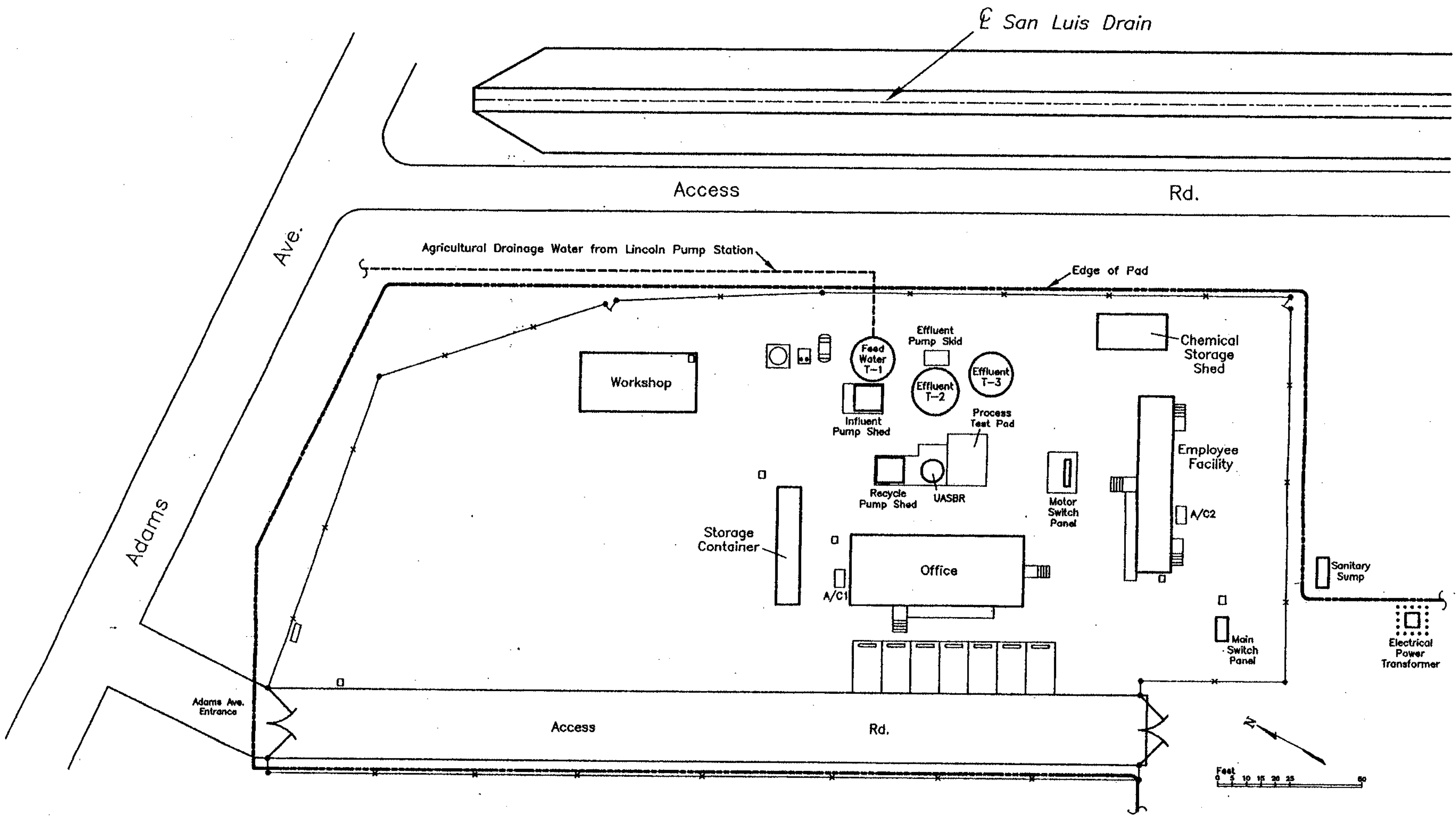

Figure 3. Adams Facility Infrastructure Plan

facility. These processes were a sequencing batch reactor, a packed bed reactor, a slow sand filter, and an upflow anaerobic sludge blanket reactor. The reactors were operated to determine the source of carbon (methanol and acetate), the residence time, and the effect of pH on selenium reduction and system operations. Actual agricultural drainage water from WWD's drain 136.0 was trucked onto the CSUF campus for use in these investigations.

The results of the laboratory-scale investigations provided basic information required for start-up. Two 30-gallon sequencing batch reactors were operated in parallel; one was fed with methanol as the carbon source, while the other was fed with acetate. Even though reduction of soluble selenium reached 86 percent and 90 percent for the methanol and acetate reactors respectively, testing showed that the SBR process was not well suited for further development on a larger scale. Selenium reduction that occurred was a result of attached-growth bacteria. The scale-up from the 30-gallon SBRs to the planned 1,000-gallon SBR predicted a lower treatment efficiency. Testing of the SBR process was terminated and replaced with testing of a continuous-flow packed bed reactor process.

Two 10-liter packed bed reactors were operated in parallel. The PBRs were operated for approximately 230 days and methanol was the carbon source. From test day 121, the PBRs reduced 77 percent and 81 percent of soluble selenium with an empty bed contact time of about 24 hours. Selenium profiles performed on the PBRs showed that selenium reduction occurred early in the reactor and that the remaining reactor volume did not provide any additional reduction.

Slow sand filtration was tested in two experiments to investigate the process as a polishing step to remove particulate selenium. In the first experiment, a slow sand filter was used to treat the effluent from the methanol-fed SBR. The second experiment consisted of testing two filters in parallel treating the effluent of the PBRs at different hydraulic loadings. For the first experiment, 67 percent of particulate selenium was removed. This percentage was calculated from the average influent and effluent selenium values for the duration of the experiment. The second experiment removed particulate selenium in both filters by 72 percent and 78 percent for hydraulic loadings of 0.04 gpm/ft^2 (0.1 m^3/(m^2*hr)) and 0.02 gpm/ft^2 (0.05 m^3/(m^2*hr)), respectively. Besides removing particulate selenium, both SSFs reduced selenium by 89 percent.

For the upflow anaerobic sludge blanket process, treatment occurs from biological reduction reactions as influent drainage water passes upwards through a sludge blanket. Retention of the sludge in the reactor is critical to the process. In addition, the chemistry of drainage water changes as it passes through the reactor, where it may cause precipitation of salt in the reactor, inhibit treatment, and lead to maintenance problems.

Lastly, two laboratory-scale upflow anaerobic sludge blanket reactors were operated to address sludge granule (biomass) retention and salt precipitation concerns and determine the efficacy of bakery sludge in reducing and removing selenium from drainage water. The lab-scale UASBRs consisted of 1-liter Imhoff cones. The sludge used in the tests was obtained from a dormant anaerobic treatment process that treated bakery waste. Methanol and potassium phosphate (to prevent nutrient deficiency) were added to the feed water for both reactors. To address the salt precipitation concern, hydrochloric acid was added to the feed of one reactor to adjust the pH from around 8 to 6.9. Both reactors were operated with a recycle flow for over 100 days at a retention time of approximately 18 hours. Water analyses indicated both reactors completely denitrified the drainage water. Around day 40 of the test, the sludge granules of the pH-adjusted reactor broke down into floc. The floc aggregated into clumps and floated to the surface. As a result of the formation of the floc, and to maintain the biomass in the reactor, the recycle flow for the reactor was terminated for the remainder of the test. Selenium reduction, based on soluble selenium of the effluent for the entire testing period, averaged 86.8 percent for the pH-adjusted reactor, while the non-pH-adjusted reactor averaged 83.4 percent. No signs of salt precipitation were observed in either reactor.